



## Short communication

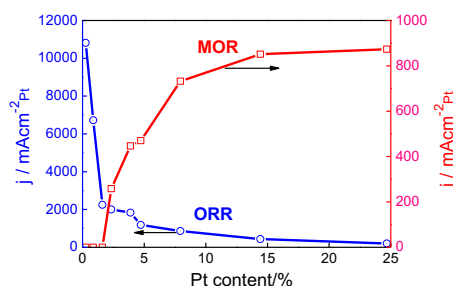
## An opposite change rule in carbon nanotubes supported platinum catalyst for methanol oxidation and oxygen reduction reactions

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## HIGHLIGHTS

- A series of carbon nanotubes supported Pt (Pt/CNTs) with same size of Pt are prepared.
- Oxygen reduction (ORR) and methanol oxidation (MOR) reactions are studied contrastively.
- Pt/CNTs show an opposite change rule for ORR and MOR along the different Pt loadings.
- The proton transfer is the key factor to determine the MOR activity.
- The reasons for the intrinsic difference between for ORR and MOR are revealed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The electrocatalytic performances of carbon nanotubes supported platinum (Pt/CNTs) with different Pt loadings for oxygen reduction reaction (ORR) and methanol oxidation (MOR) are studied contrastively. Pt/CNTs showed an opposite change rule along different Pt loadings for ORR and MOR, which is discussed based on the charge transportation and mass transfer. The results show that at low Pt loading, proton conduction is the key factor, which determines the MOR activity; at high Pt loading, mass transfer is crucial, which decides the ORR activity of Pt/CNT catalysts. The viewpoint proposed in this paper can guide the design and preparation of Pt based catalysts for the commercialization of direct methanol fuel cells.

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## 1. Introduction

Direct methanol fuel cells (DMFCs), as a clear and efficient electrochemical energy conversion system, have received much attention with a wide range of potential application. In the recent twenty years, although tremendous efforts have been devoted to

develop the alternative catalysts due to the Pt scarcity and cost, generally speaking, in acidic medium, Pt and Pt-based catalysts are still the most practical oxygen-reduction reaction (ORR) and methanol-oxidation reaction (MOR) catalysts at the current stage of technology [1,2]. Besides the scarcity and the cost, another drawback with Pt-based catalyst for DMFC is the methanol diffusion across the membrane to cathode, which causes significant deterioration of cathode performance due to the mixed potential caused by the two simultaneous reactions of ORR and MOR at the cathode.

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Because Pt possesses good catalytic activity for ORR and MOR, it seems impossible for Pt based catalyst to eliminate this drawback. However, in our recent work, we found an interesting phenomenon [3]. The carbon nanotube supported Pt catalyst (Pt/CNT) showed high activity for ORR but had hardly activity for MOR when the Pt loading was lower than 1 wt%, which means that Pt catalyst has selectivity for ORR and MOR when designed rationally. This inspired us to acquire deeper insights into the reasons for Pt showing such intrinsic difference for MOR and ORR, which is very crucial for the design of Pt-based catalyst for the commercialization of DMFC.

In this work, a series of Pt/CNT catalysts with different Pt loadings were prepared. Their morphologies and activities for ORR and MOR were investigated. The reasons for the intrinsic difference between for ORR and MOR were revealed.

## 2. Experimental

CNTs were provided by Shenzhen Nanotech Port Co., Ltd. Before use, it was treated by a well-known acid oxidation method to introduce oxygenous groups for the subsequent immobilization of Pt. Pt/CNTs catalyst was prepared as follows [4]. Treated CNTs were added to ethylene glycol under constant stirring for 10 min. Then appropriate amounts of  $\text{H}_2\text{PtCl}_6$  and KOH were added with constant stirring. The slurry was refluxed at 140 °C for 2 h to ensure the complete reduction of Pt (IV). The solid product was rinsed repeatedly with deionized water, and dried in vacuum at 70 °C for 12 h. For comparison, 5%  $\text{RuO}_2/\text{CNTs}$  were prepared [4], and then Pt was deposited on  $\text{RuO}_2/\text{CNTs}$  with the same procedure as Pt/CNTs to obtain Pt/ $\text{RuO}_2/\text{CNTs}$  (1 wt% Pt). The as-prepared Pt/CNTs (14.4 wt% Pt) were diluted homogeneously with the above treated CNTs to obtain Pt/CNTs-D (1 wt% Pt).

Electro-Probe Microanalyzer (EPMA, EPMA-1600, Shimadzu Corporation) was used to determine the content of Ru and Pt in the catalyst. High resolution transmission microscopy (HTEM, JOEL, JEM-2010HT) was used to characterize the morphology of the catalysts.

Electrochemical measurements were carried out at room temperature in a three-electrode cell connected to computer-controlled

Autolab PGSTAT30 electrochemical analyzer (Eco Chemie B. V., Utrecht, Netherlands). The preparation of electrodes was described in our previous paper in detail [5]. A glass carbon electrode coated with 0.02 mg catalyst was used as the working electrode. An Ag/AgCl electrode and a Pt electrode were used as reference and counter electrodes, respectively. Cyclic voltammogram (CV) curves for ORR were recorded in 1 M  $\text{O}_2$ -saturated  $\text{HClO}_4$  solution with a scan rate of 100  $\text{mV s}^{-1}$ . The MOR activity was measured also by CV in 1 M  $\text{CH}_3\text{OH}$  with 1 M  $\text{HClO}_4$  as electrolyte at 25 °C with a scan rate of 100  $\text{mV s}^{-1}$ . For the electrochemical active surface area (EAS) measurement, the CV curve of pre-adsorbed CO electro-oxidation was recorded from –220 to 900 mV versus Ag/AgCl [6].

## 3. Results and discussion

Fig. 1 shows the HTEM images and particle size distributions of Pt/CNTs with different Pt loadings. It can be seen that the density of Pt nanoparticles on the surface of CNTs increased with the Pt loading increasing. While the size of Pt nanoparticles changed little ranging from 3.41 to 3.68 nm for Pt loadings from 0.87 wt% to 14.42 wt%, indicating the effect of particle size on activity may be excluded.

The electrocatalytic activities of ORR and MOR of the Pt/CNTs with different Pt loadings were tested by CV. The transformation CVs based on mass of Pt loaded on electrode for ORR and MOR were shown in Figs. 2 and 3, respectively. It was proven that CNTs performed no ORR activity without Pt deposition in acidic medium [3]. Fig. 2 shows the 0.26%-Pt/CNT catalyst possessed outstanding ORR peak current of 5.1  $\text{A mg}^{-1}_{\text{Pt}}$ , which is five times as much as that of Pt nanoparticles with a diameter of 3 nm that had the maximum mass activity reported by Perez-Alonso et al. [7]. However, from Fig. 3, it can be seen that Pt/CNT catalysts with Pt loadings of 0.26 wt% and 0.87 wt% showed no MOR activity. The MOR activity began to appear and increase when the Pt loading was larger than 2.33 wt% and then became stable with the Pt loading further increasing. For clarity, the relationship between the electrocatalytic activities of ORR and MOR and the Pt loadings were shown in Fig. 4. From Fig. 4, it can be seen that the variation of curves based on the mass-specific activity agrees well with that of based on EAS-specific

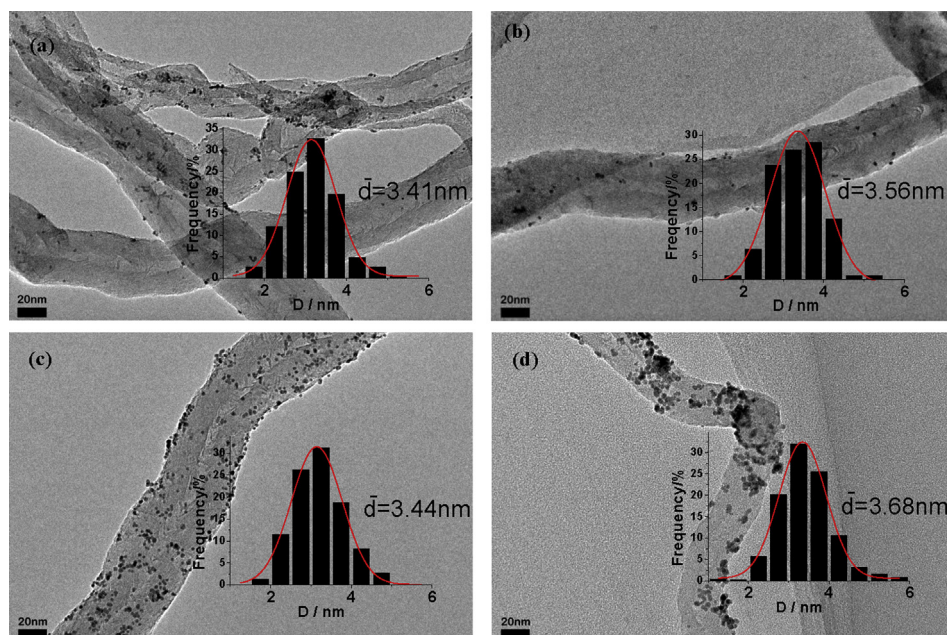
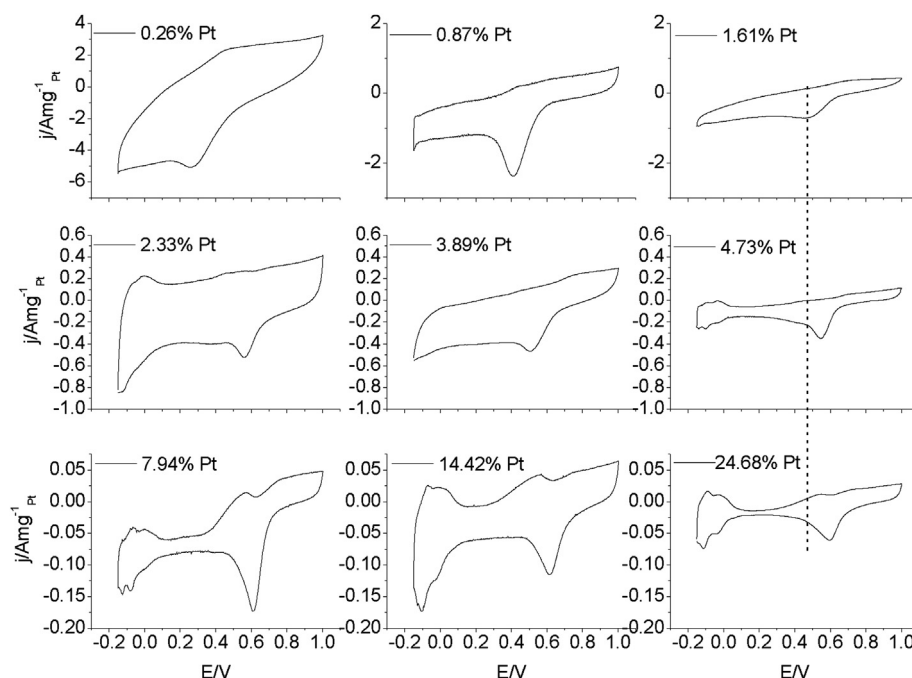


Fig. 1. TEM photos of Pt/CNTs with different Pt loadings: (a) 0.87%, (b) 1.61%, (c) 4.73% and (d) 14.42%.



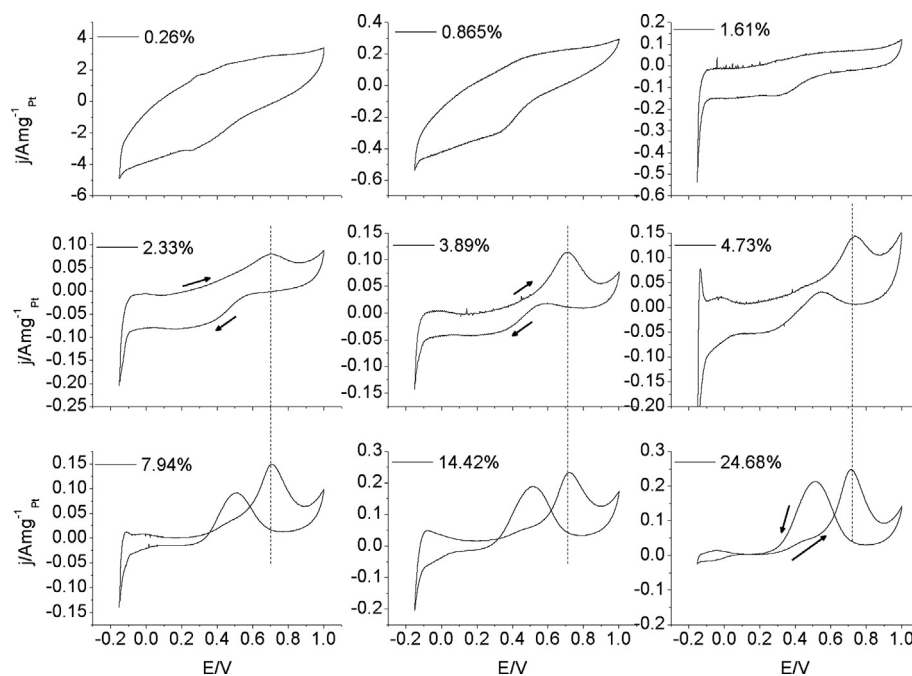
**Fig. 2.** Cyclic voltammograms (ORR) of Pt/CNTs with different Pt loadings in 1 M HClO<sub>4</sub> O<sub>2</sub>-saturated solution.  $j$ -the current density based on mass of Pt loaded on electrode. The broken line indicates the change of the peak potentials.

activity for ORR and MOR along the different Pt loadings, further indicating the same size of Pt nanoparticles for different Pt/CNTs. However, it is surprising that Pt/CNTs showed an opposite change rule for ORR and MOR, which means that the intrinsic factor influencing the ORR and MOR activities is different.

The TEM result demonstrates the effect of particle size on the activity can be excluded. Therefore, there are other factors influencing the ORR and MOR need to be considered. Based on the possible steps of ORR and MOR, both electron and proton are

involved in the ORR and MOR [5,8–11]. So, electron and proton transfer may have influence on ORR and MOR, especially at lower Pt loading, where the distance of Pt nanoparticles is rather large.

As is well known, carbon nanotube is excellent conductor for electron transfer but not good for proton conduction. So, carbon nanotube is responsible for the electron transfer. Nevertheless, for proton conduction, proton needs to adsorb onto the Pt nanoparticles first and then to diffuse through Pt nanoparticles. So the distance of Pt nanoparticles has an important impact on its proton



**Fig. 3.** Cyclic voltammograms (MOR) of Pt/CNTs with different Pt loadings in 1 M HClO<sub>4</sub> and 1 M CH<sub>3</sub>OH.  $j$ -the current density based on mass of Pt loaded on electrode. The broken lines indicate the change of the peak potentials.

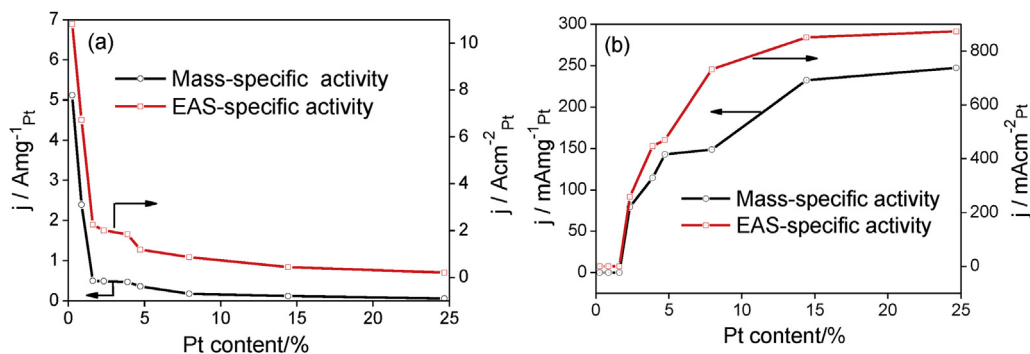


Fig. 4. The specific activities of Pt/CNTs with different Pt loadings for (a) ORR and (b) MOR. The current densities ( $j$ ) of MOR come from the forward anodic peak current in CVs.

conductivity. Under lower Pt loadings (0.26 wt% and 0.87 wt%), the distance of Pt nanoparticles was too large to transport the proton produced during methanol deprotonation, which caused the oxidation process to be interrupted, showing almost no MOR activity. With the increase of Pt loading, the density of Pt nanoparticles increased, the distance of Pt nanoparticles became closer, and the ability of proton transport enhanced, resulting in the appearance and enhancement of MOR activity. While in ORR, proton from the anode is abundant, the electron transfer is very important factor. Because of the good conductivity of CNTs, the electron involved in ORR could be transported efficiently, even in very low Pt loading, Pt/CNTs showed high ORR specific-activity.

However, from Fig. 4(a), it can be seen that the mass-specific activity for ORR decreased rapidly with the increase of Pt loading. In fact, the ORR peak current detected on the glass carbon electrode (Fig. S1) increased with the increase of Pt loading from 0.26% to 0.87%, and then kept almost stable when the Pt loading increased from 0.865% to 24.68%, resulting that the current density based on

mass of Pt loaded on electrode (mass-specific activity) decreased dramatically. It is clearly indicated that ORR was controlled by the mass transfer. As expected, when the dosage of Pt catalyst on the electrode decreased, the ORR peak current did not proportionally decreased (Fig. S3a), but the mass-specific activity increased linearly (Fig. S3b), confirming that the mass transfer was the key factor for ORR. Interestingly, the peak potential for ORR increased gradually with Pt loading of catalyst increasing (Fig. 1), likewise, the potential also increased gradually with the dosage of Pt on electrode increasing (Fig. S3a). We suggest that the peak potential for ORR is correlation with the interaction between the active sites and support. The interaction of Pt and carbon nanotubes was changed with the Pt loading increasing, as a result the peak potential increased with the Pt loadings. For MOR, Fig. S3c,d show that the peak current proportionally increased with the dosage of Pt catalyst increasing, but the mass-specific activity remained almost stable, indicating that the mass transfer was not the limiting factor for MOR. Moreover, the peak potential for MOR also kept unchanged

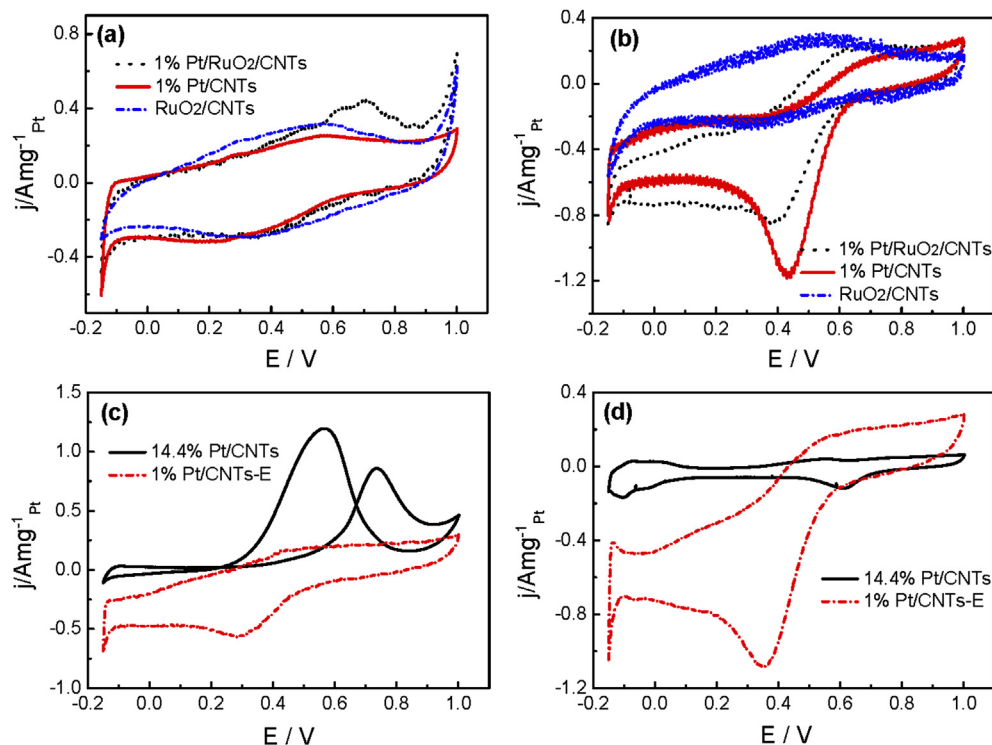


Fig. 5. (a) and (c) Cyclic voltammograms of different catalysts in 1 M  $\text{HClO}_4$  and 1 M  $\text{CH}_3\text{OH}$  (MOR). (b) and (d) Cyclic voltammograms of different catalysts in 1 M  $\text{HClO}_4$   $\text{O}_2$ -saturated solution (ORR).



obviously under different dosage of Pt catalyst (Fig. S3c), as different Pt loading of catalyst (Fig. 2). It means the peak potential for MOR was not affected by the interaction between the active sites and support. It was determined by the intrinsic properties of active metal, and therefore the peak potentials for MOR on Pt/CNTs catalysts with different Pt loadings were similar.

In order to further confirm the effects of proton conduction and mass transfer on MOR and ORR, Pt/RuO<sub>2</sub>/CNTs (1 wt% Pt) and Pt/CNTs-D (1 wt% Pt) were prepared and their MOR and ORR were compared with Pt/CNTs, as shown in Fig. 5. RuO<sub>2</sub> is a good proton conductor [4,12,13], while it is inactive to ORR and MOR. Due to the improved proton conductivity, Pt/RuO<sub>2</sub>/CNT catalyst showed obvious methanol oxidation peak compared with Pt/CNT with the same Pt loading, which was no activity for MOR, indicating that proton conductivity enhanced MOR activity (Fig. 5(a)). While for Pt/CNTs-D, no MOR activity was shown due to its proton transfer impairing, although the Pt nanoparticles in Pt/CNTs-D is the same as in Pt/CNT (14.4% Pt) catalyst that showed rather high MOR activity (Fig. 5(c)). So, it can be concluded that proton transfer is the key factor, which determines the MOR activity of Pt based catalyst at low Pt loading. On the other hand, Pt/RuO<sub>2</sub>/CNTs showed a little decreased ORR activity compared with Pt/CNTs with the same Pt loading due to the cover of RuO<sub>2</sub> on CNTs (Fig. 5(b)), but its ORR activity was still high due to the good electron conduction of CNTs. Compared with Pt/CNTs (14.4 wt% Pt), Pt/CNTs-D (1 wt% Pt) showed significantly enhanced ORR mass-specific activity (Fig. 5(d)) due to its mass transfer effect, which is consistent with the result discussed above on catalyst dosage and Pt loading. So, it can be deduced that mass transfer is crucial, which decides the ORR activity of Pt/CNT catalysts at high Pt loading.

#### 4. Conclusions

An opposite change rule along different Pt loadings in Pt/CNTs for ORR and MOR was revealed based on the charge transportation and mass transfer. At low Pt loading, proton conduction is the key

factor, which determines the MOR activity. At high Pt loading, mass transfer is crucial, which decides the ORR activity of Pt/CNT catalysts. The viewpoint proposed in this paper is important and useful, which can guide the design and preparation of Pt based catalysts for DMFC.

#### Acknowledgments

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.03.001>.

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